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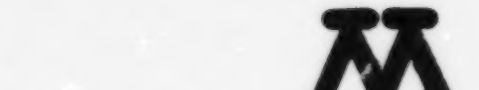

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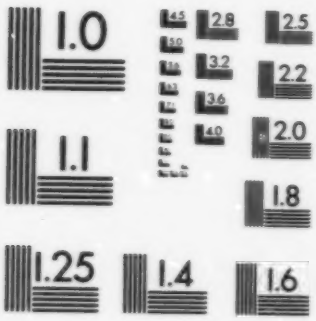

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KINETIC STUDIES OF COKE FORMATION IN HYDROCARBON FRACTIONS OF DIFFERENT BITUMENS UNDER VARIOUS CONDITIONS (PHASE III)

FINAL REPORT

by

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PREFACE

Under the terms of the contract between the Department of Energy, Mines and Resources and the University of Ottawa, kinetic studies were to be made of coke formation from hydrocarbon fractions of bitumens and heavy oils. The experimental program was divided into three tasks:

I Separation of four feedstocks, to be supplied by the scientific authority (Dr. B.N. Nandi), into asphaltene, soft resin, hard resin, saturates and aromatics.

II A study of the kinetics of coke formation from at least three of the feedstocks themselves, and from the corresponding asphaltenes and soft resins, in an atmosphere of hydrogen.

III A study of the kinetics of coking in the presence of hydrogen sulphide.

Since Dr. Banerjee withdrew from the project on October 15, 1986, it was not possible for work to be done on Task III. The present report therefore covers Tasks I and II only.

ABSTRACT

The following four heavy crudes were separated into fractions:

1) Interprovincial Pipeline vacuum bottom (+ 1050°F) — 30-IPPL-84
2) Interprovincial Pipeline vacuum bottom (+ 900°F) — 31-IPPL-84
3) Athabasca bottom product (+ 977°C) — 26-AB-81 (44-1)
4) Athabasca straight bitumen — 26-AB-81

Each was separated into asphaltene, soft resin, hard resin, aromatics and saturates. Elemental analyses were carried out on the fractions.

For the first three of the above crudes, and their fractions, rate measurements were made of coke formation in an atmosphere of hydrogen at a pressure of 15 MPa (2250 p.s.i.), and at different temperatures.

As in our previous investigations, the rates of coke formation were significantly higher for the asphaltenes than for the resins. Little coke was obtained from the aromatics and saturates. There is some correlation between aromaticity and rate of coke formation, but structural effects also play a role. The rates of coke formation from the heavy crudes are correlated with the percentages of asphaltene and resins present in them. Athabasca crude and its fractions shows significantly different behaviour from that shown by the Pipeline crudes and their fractions.

INTRODUCTION

The upgrading of heavy oils is always accompanied by the formation of substantial amounts of coke. Today there are increasing commercial demands for the lighter hydrocarbons, and hydrocracking processes are commonly used for liquefying coal and oils, with the formation of lower boiling products. Coke production during these processes presents practical difficulties, and attempts are being made to minimize it. Such attempts will be helped by kinetic studies, which lead to conclusions about the mechanism of coke formation.

In previous reports and publications [1-4] we have described detailed kinetic studies of coke formation under various conditions. Heavy crudes have been broken down into fractions, and studies made of the kinetics of coke formation from these fractions as well as from the original crudes. The work has been done in atmospheres of nitrogen and of hydrogen.

Coke formation is a complex process, involving a number of stages. The previous work has indicated that both simultaneous (parallel) and consecutive reactions are playing important roles, some of the evidence for this coming from the type of temperature dependence observed [1-4]. We have proposed a tentative reaction mechanism which appears to explain the main effects observed.

In addition, the upgrading of heavy crudes has been the subject of many other investigations. Recently Gould and Long [5] proposed that in the presence of a catalyst the basic component of oil interacts with the catalyst, and suggested that this might be the cause of coke formation during upgrading processes. Phillips et al. [6] studied bitumen in the presence of sand, and determined the amount of coke in the product. Obara et al. [7] studied the carbonization behaviour of pitch in the presence of inert material. Inagaki et al. [8] investigated the influence of the molecular weight of different

fractions of coal-tar pitch on the carbonization behaviour under pressure.

OBJECTS OF THE PRESENT WORK

Our previous report [2], and a journal publication [3], described the kinetics of coke formation from Cold Lake and Arabian heavy crudes, and some of their fractions, under an atmosphere of hydrogen. The present work extends this investigation to Interprovincial Pipeline heavy crudes and Athabasca bitumen. These materials were separated into their fractions, and the kinetics of coke formation were studied in an atmosphere of hydrogen at high pressure.

The following heavy crudes were supplied to us by CANMET:

(1) Interprovincial pipeline vacuum bottom (+ 1050°F) — 30-IPPL-84

(2) Interprovincial pipeline vacuum bottom (+ 900°F) — 31-IPPL-84

(3) Athabasca bottom product (+ 977°F) — 26-AB-81 (44-1)

(4) Athabasca straight bitumen — 26-AB-81

PART I: SEPARATION OF HEAVY CRUDES INTO FRACTIONS

The experimental procedures used for the separations were the same as those described in detail in the previous report [2]. For convenience their essential features are summarized in Appendix A to the present report.

Analyses

Speight [10] described in detail various analyses of petroleums and related materials. In the present work IR, NMR and elemental analyses were used to characterize the fractions obtained by chromatographic procedures.

NMR Spectroscopy

The 1H FTNMR spectra, in CCl_4 solution, were taken with the asphaltene fractions of Interprovincial Pipeline heavy crudes, and the results are shown in Figures 1 and 2. Detailed FTNMR studies were not made, since it was not considered that they would provide additional information.

Structural studies of the asphaltene fraction of Athabasca bitumen were carried out using 13C FTNMR spectroscopy, all of the spectra being taken in $CDCl_3$ solution. A typical spectrum is shown in Figure 3; the same fractions from different bitumen sources showed very similar spectra.

The NMR spectra of the fractions show a strong band near 7.2 δ; this corresponds to aromatic hydrogen atoms. The sharp bands between 1 and 2 δ are due to aliphatic protons. The signal at 0.9 δ shows paraffinic methyl protons, whereas that at 1.35 δ is due to protons from methylene groups. The signal in the 1.8 to 2.2 δ region may be due to naphthenic protons. The bands in the aromatic fractions are due to aliphatic side chains. The signal near 2.5 δ, present only in the aromatic fraction, is due to the methyl group attached to the aromatic rings.

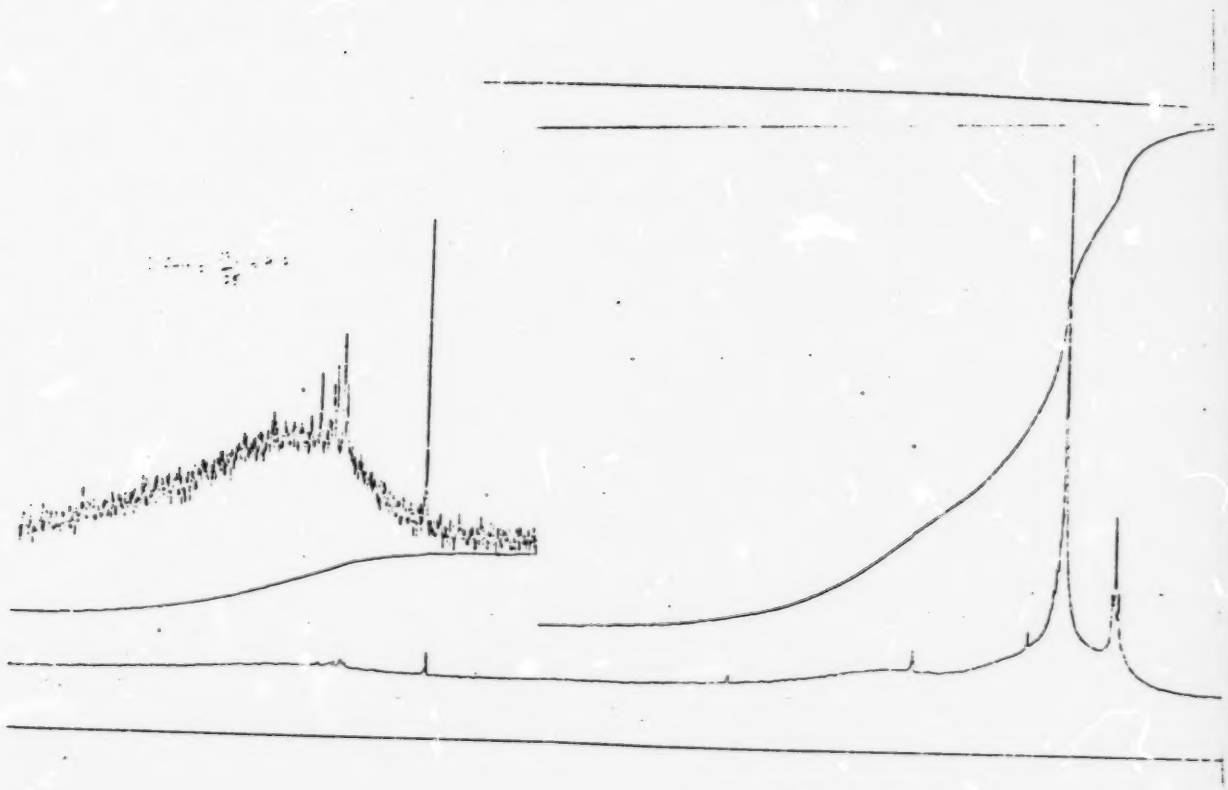

FIGURE 1: 1H FTNMR spectrum of asphaltene from 30-IPPL-84 bitumen

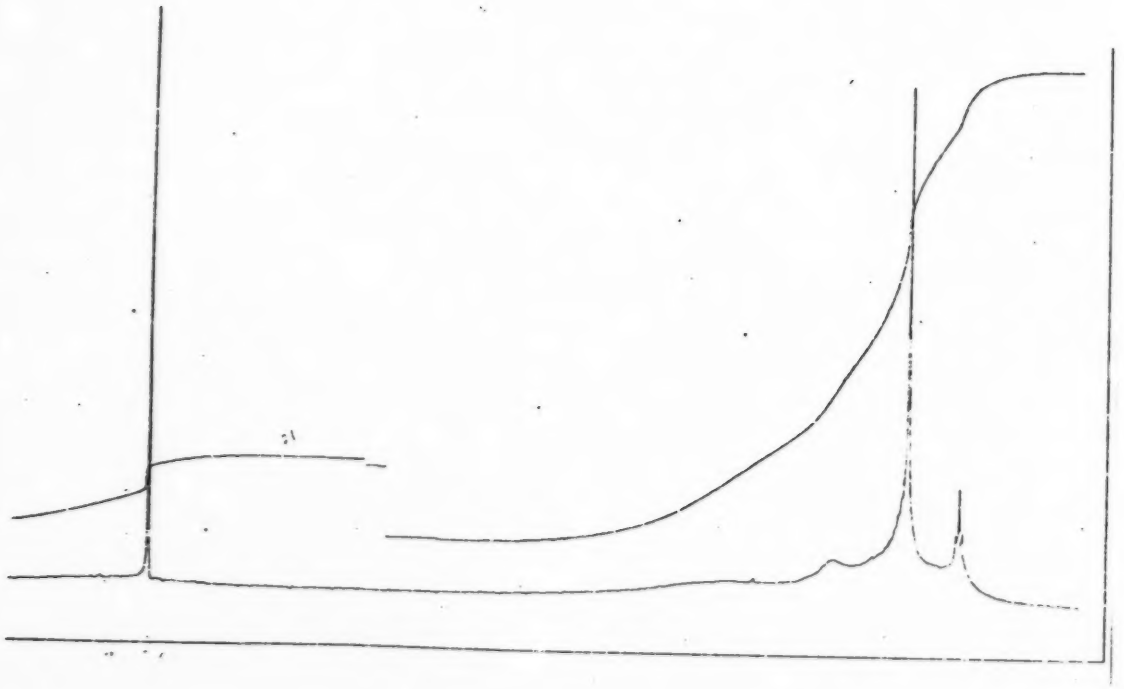

FIGURE 2: 1H FTNMR spectrum of asphaltene from 31-IPPL-84 bitumen

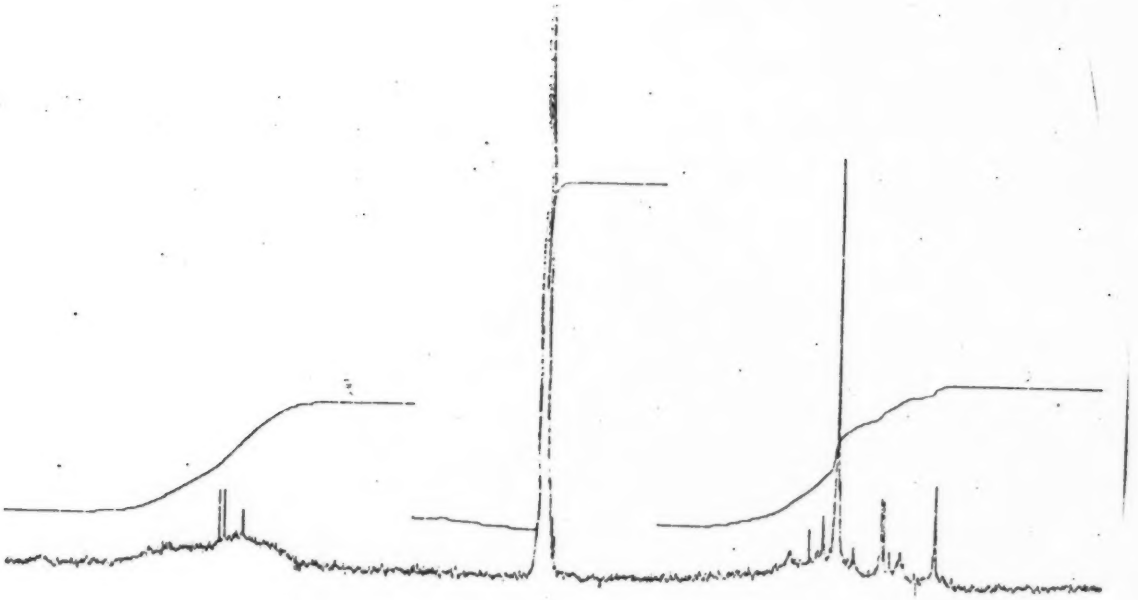

FIGURE 3: 13C FTNMR spectrum of asphaltene from Athabasca bitumen

Infrared Spectroscopy

IR spectra were taken in carbon tetrachloride solution, and typical spectra of different fractions from Interprovincial Pipeline heavy crudes are show in Figures 4 to 11.

The IR spectra provide important information about some functional groups. Strong bands at 1600 cm^{-1} and 800 cm^{-1} indicate $-CH_2-$ groups in cyclic structures. A broad band in the region of 3500 to 3000 cm^{-1} is due to a hydrogen-bonded OH or NH group. The 1660 cm^{-1} band in the soft resin represents a free CO group. Bands in the region 1300-1200 cm^{-1} indicate that oxygen is present in an ether linkage between two aromatic rings. The band in the 1600-1500 cm^{-1} region suggests nitrogen in the form of amide. The sharp band near 1000 cm^{-1} may be due to sulphur present in S O.

Elemental Analyses

The elemental analyses of the heavy crudes were carried out by CANMET, and the results supplied by them are reproduced in Tables 1-4.

Table 5 shows the percentage yields of the major fractions. The elemental analyses for the fractions separated from the heavy crudes are presented in Table 6.

Discussion

Tables 1 to 4 show that the Interprovincial Pipeline heavy crude 31-IPPL-84 has the highest API gravity (10.43) and the Athabasca vacuum bottom the lowest (0.37). Elemental analyses show that the H/C ratio is low for Athabasca vacuum bottom (1.36) and highest for 31-IPPL-84 (1.51). This shows that Athabasca vacuum bottom is the most aromatic of the four feedstocks.

It was found that Athabasca heavy crudes are sulphur rich (more than 3%) as compared to the IPPL heavy crudes (less than 3%).

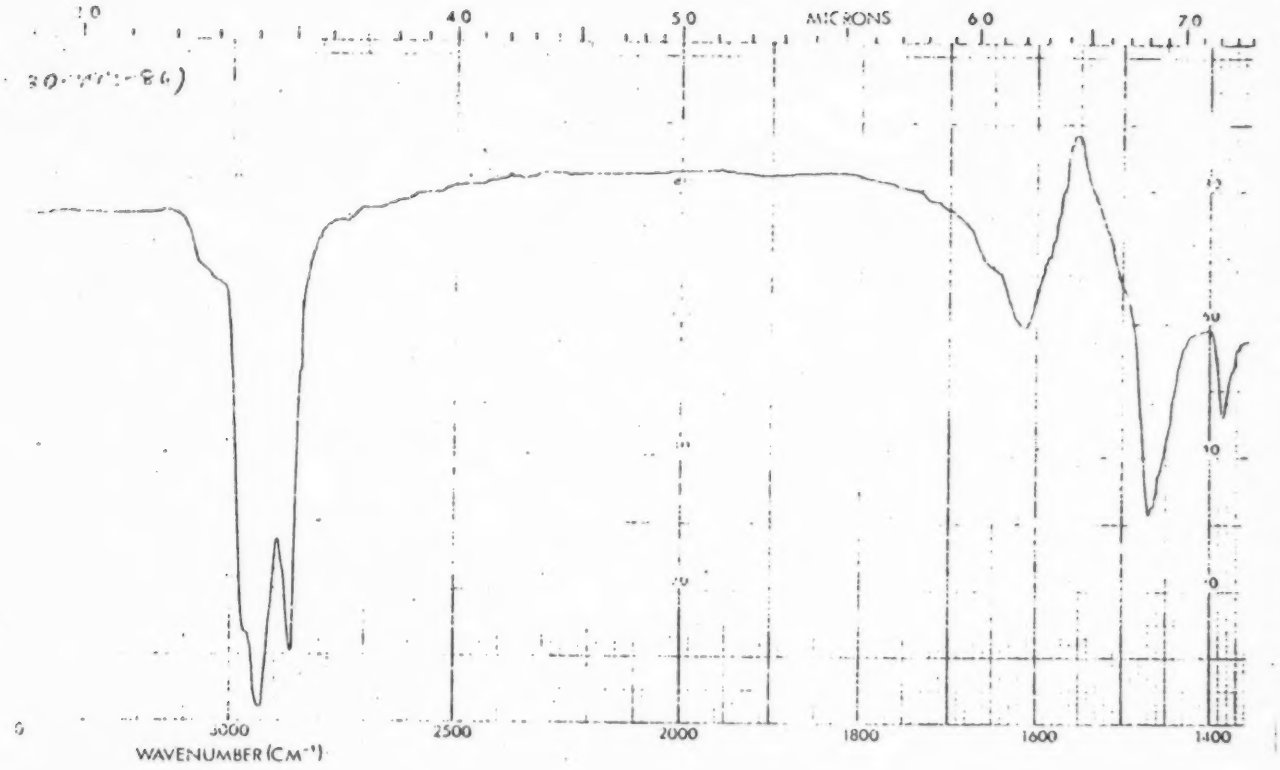

FIGURE 4: Infrared spectrum of asphaltene from 30-IPPL-84 bitumen

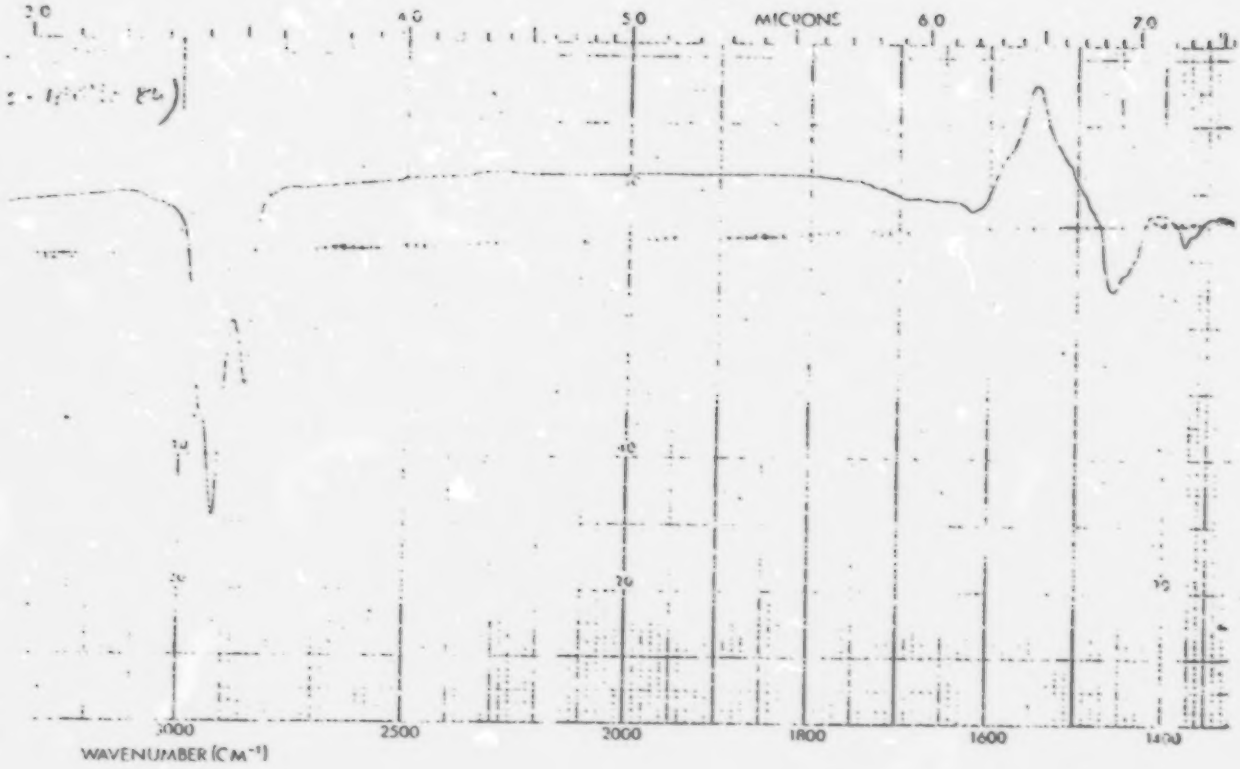

FIGURE 5: Infrared spectrum of hard resin from 30-IPPL-84 bitumen

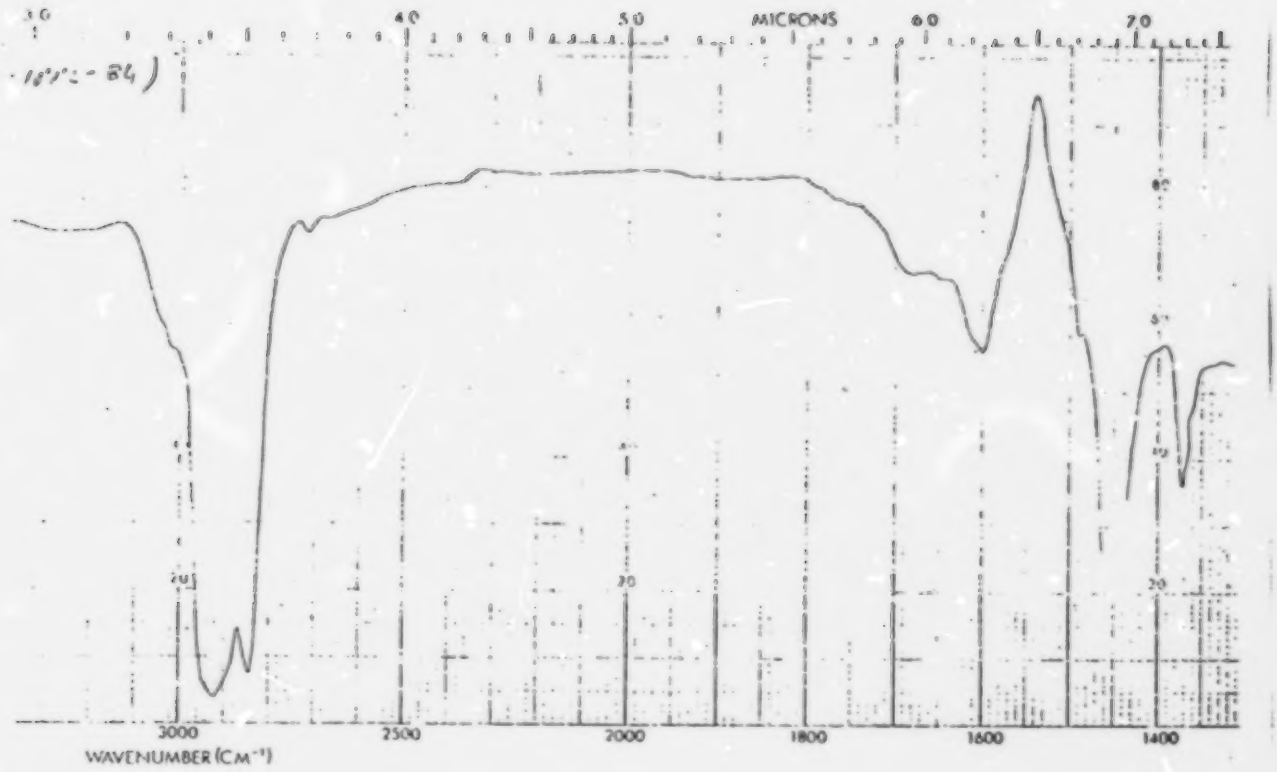

FIGURE 6: Infrared spectrum of soft resin from 30-IPPL-84 bitumen

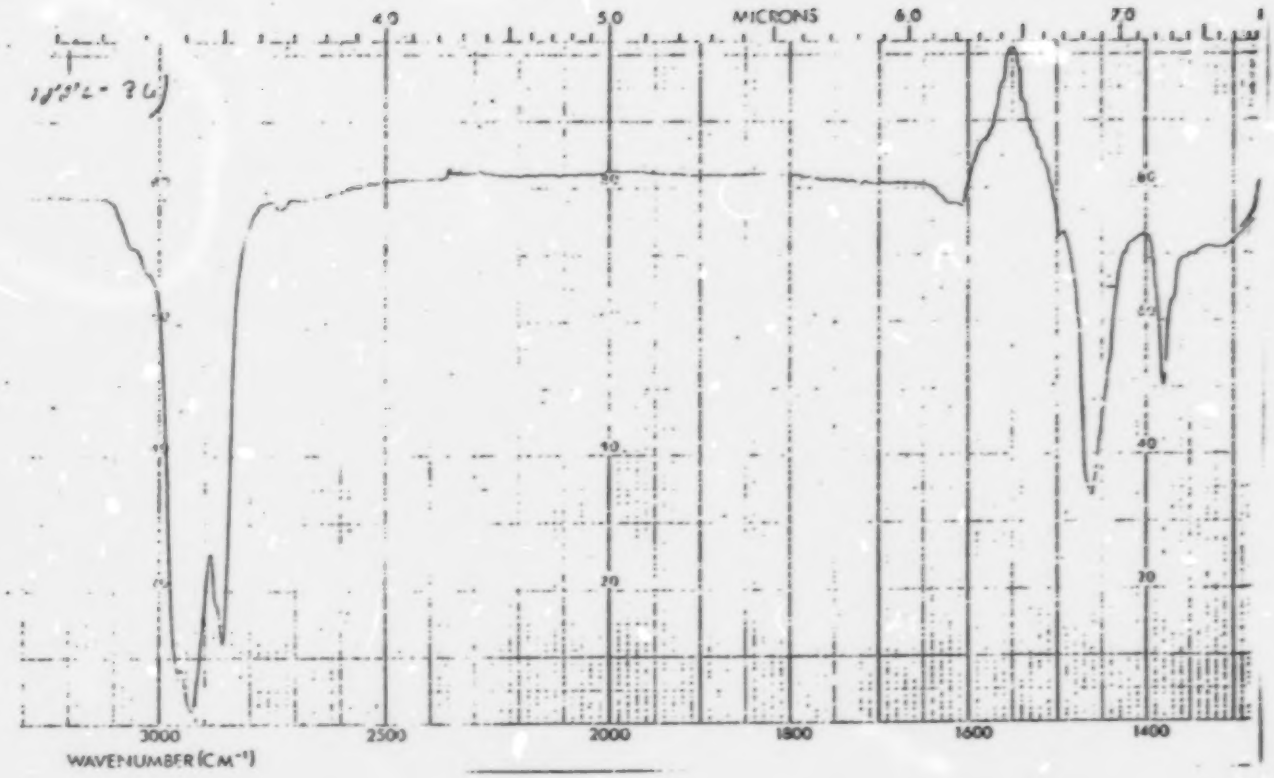

FIGURE 7: Infrared spectrum of aromatics from 30-IPPL-84 bitumen

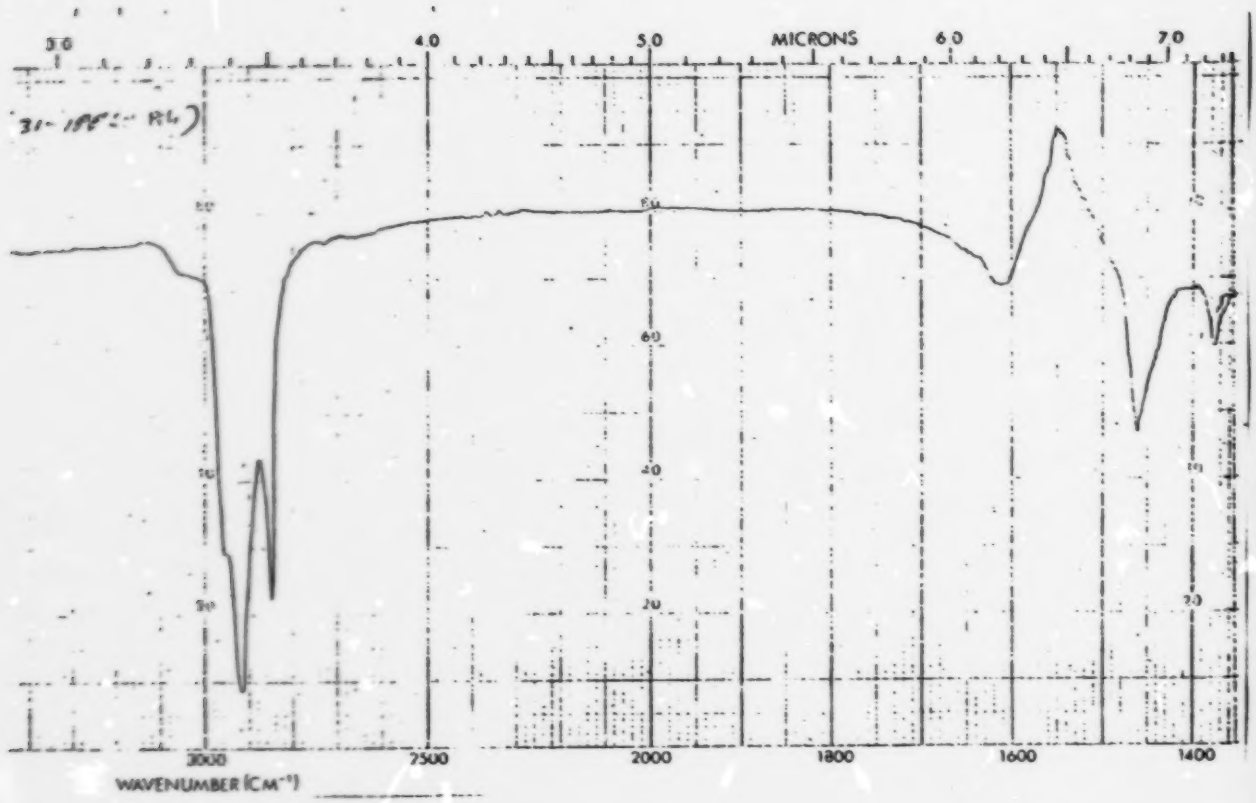

FIGURE 8: Infrared spectrum of asphaltene from 31-IPRL-84 bitumen

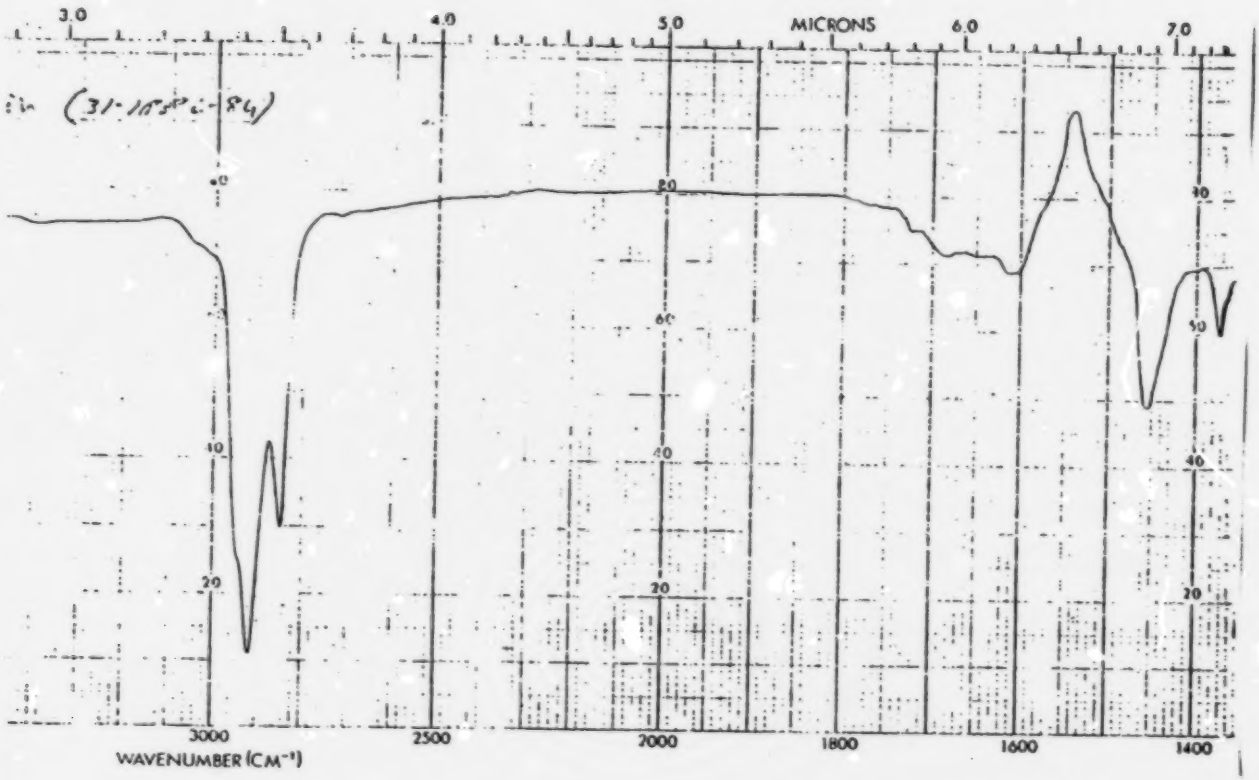

FIGURE 9: Infrared spectrum of hard resin from 31-IPPL-84 bitumen

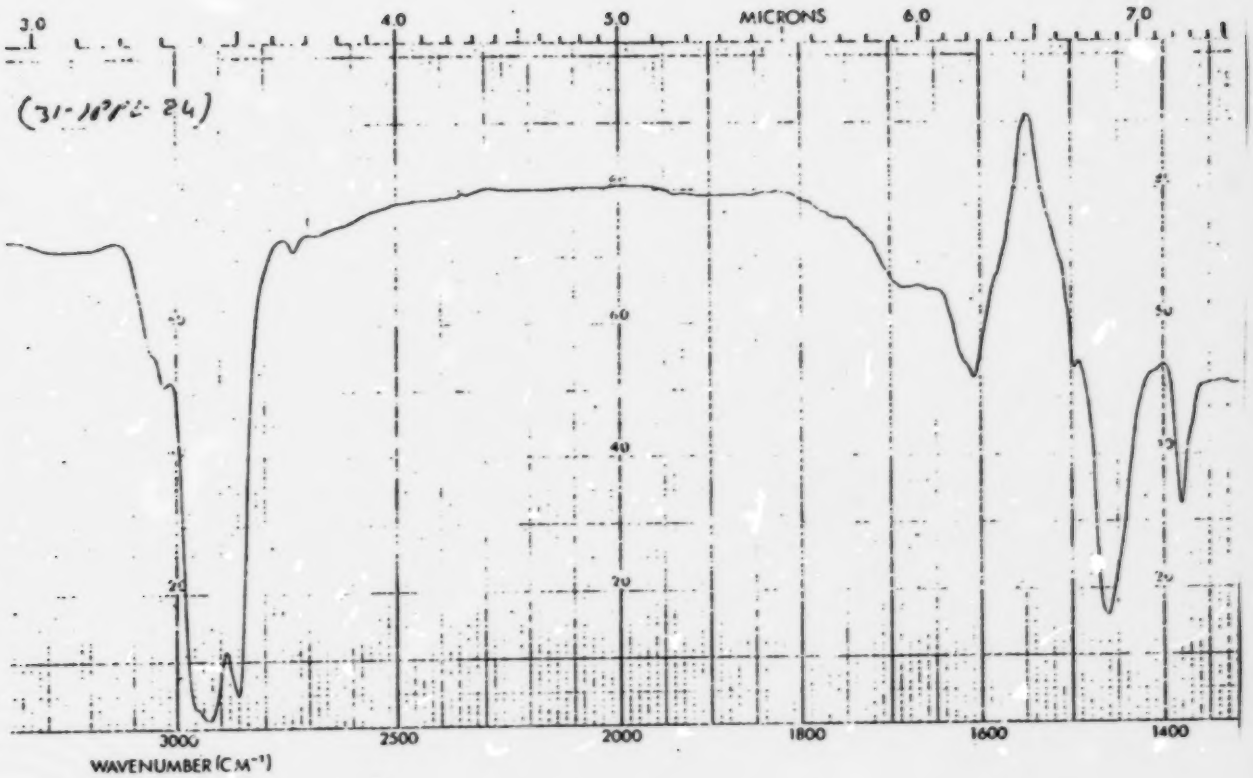

FIGURE 10: Infrared spectrum of soft resin from 31-IPPL-84 bitumen

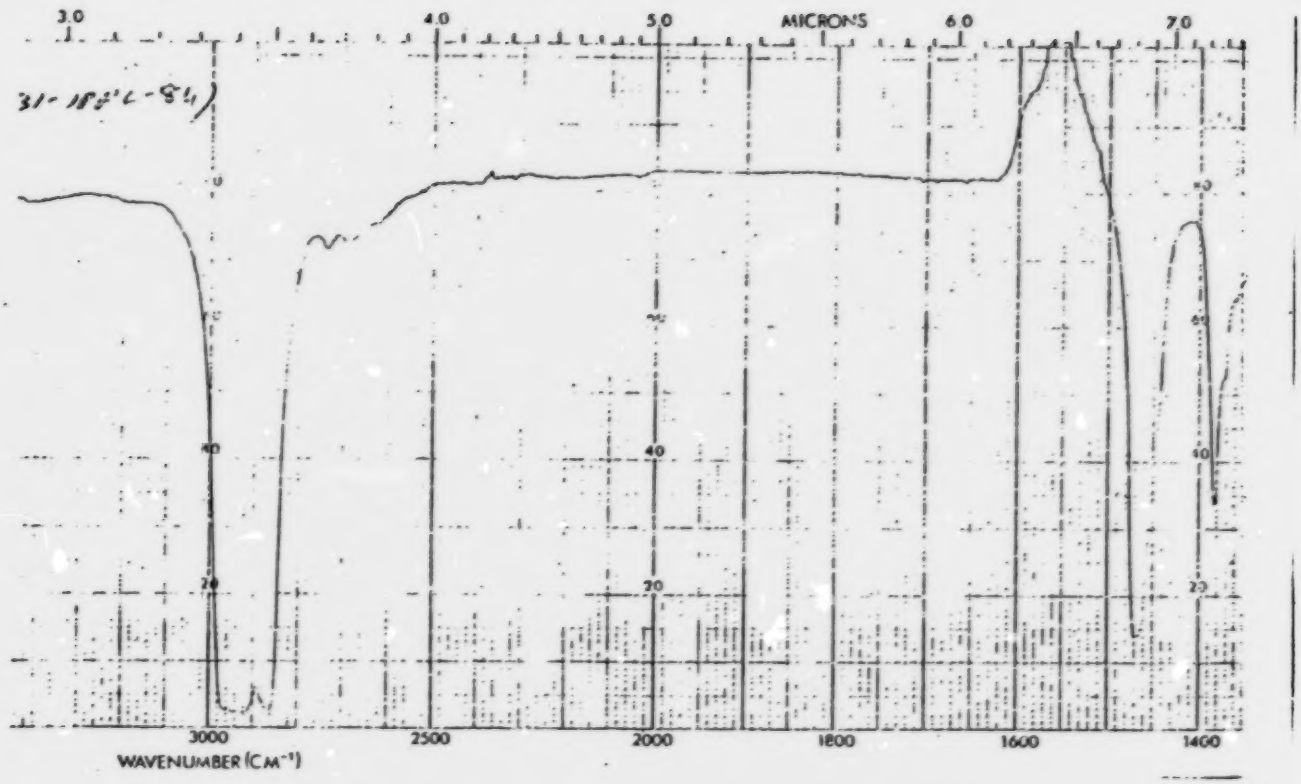

FIGURE 11: Infrared spectrum of aromatics from 31-IPPL-84 bitumen

TABLE 1

Analysis of 30-IPPL-84 Bitumen

(Lab. No. BP-320-84)

Gravity,	°API	7.36
Specific Gravity,	15/15°C	1.019
Ash,	wt%	0.04
Sulphur,	wt%	2.45
Carbon,	wt%	86.4
Hydrogen	wt%	10.2
H/C		1.41
Nitrogen,	wt%	0.47
R.C.R.,	wt%	20.4
Pentane Insolubles,	wt%	20.2
Toluene Insolubles,	wt%	0.70
Pour Point,	°C	50°C
Softening Point,	°C	49.0
Viscosity @ 100°C,	cp	1889
Viscosity @ 150°C,	cp	131.8
Heat of Combustion,	kJ/kg	42400
Vanadium,	ppm	102
Nickel,	ppm	55
Iron,	ppm	124
Titanium	ppm	3
Aluminum	ppm	53
Silica	ppm	18
Sodium	ppm	46
Potassium	ppm	31
Calcium	ppm	19
Magnesium	ppm	12

This analysis was supplied to us by CANMET

TABLE 2

Analysis of 31-IPPL-84 Bitumen

(Lab. No. BP-1422-84)

Gravity,	°API	10.43
Specific Gravity,	15/15°C	0.997
Ash,	wt%	0.02
Sulphur,	wt%	2.06
Carbon,	wt%	85.4
Hydrogen,	wt%	10.8
H/C		1.51
Nitrogen,	wt%	0.46
Oxygen,	w/w	0.24
R.C.R.,	wt%	15.4
Pentane Insolubles,	wt%	13.4
Toluene Insolubles,	wt%	0.79
Pour Point,	°C	39
Softening Point,	°C	37.5
Viscosity @ 100°C	cp	382.3
Viscosity @ 130°C	cp	95.4
Vanadium	ppm	78
Nickel	ppm	38
Iron	ppm	72
Titanium	ppm	trace
Aluminum	ppm	16
Silica	ppm	trace
Sodium	ppm	24
Potassium	ppm	10
Calcium	ppm	6
Magnesium	ppm	4

This analysis was supplied to us by CANMET

TABLE 3

Analysis of 26-AB-81 (44-1) Bitumen

(Lab. No. BP-369-82)

Gravity,	°API	0.37
Specific Gravity,	60/60°F	1.073
Ash,	wt%	1.08
Sulphur,	wt%	6.20
Carbon,	wt%	83.25
Hydrogen,	wt%	9.45
H/C		1.36
Nitrogen,	wt%	0.82
R.C.R.,	wt%	25.73, 25.66, 25.96
C.C.R.,		27.15, 27.83
Pentane Insolubles,	wt%	31.4
Toluene Insolubles,	wt%	0.86
Viscosity @ 150°F	cSt	sample would not
Viscosity @ 210°F	cSt	flow in viscometer
Vanadium	ppm	412
Nickel	ppm	156
Titanium	ppm	270
Iron	ppm	683
Copper	ppm	2
Aluminum	%	0.16
Silica	%	0.22
Sodium	ppm	56
Potassium	ppm	158
Calcium	ppm	106
Cobalt	ppm	12
Magnesium	ppm	78

This analysis was supplied to us by CANMET

TABLE 4

Analysis of 26-AB-81 Bitumen

(Lab. No. BP-97-83)

Gravity,	°API	8.88	
Specific Gravity,	15/15°C	1.008	
Ash,	wt%	0.61	
Sulphur,	wt%	4.65	
Carbon,	wt%	82.87	
Hydrogen,	wt%	10.10	
H/C		1.46	
Nitrogen,	wt%	0.48	
R.C.R.,	wt%	14.0	
Pentane Insolubles,	wt%	17.3	
Toluene Insolubles,	wt%	1.00	
Pour Point,	°C	21	
Softening Point,	°C	3.5	
Viscosity @ 130°C	cp	41.9	
Viscosity @ 70°C	cp	799.4	
Viscosity @ 100°C	cp	141.9	
Heat of combustion,	kJ/kg	41465	
Vanadium	ppm	208	197
Nickel	ppm	79	82
Iron	ppm	378	404
Titanium	ppm	123	122
Aluminum	ppm	879	887
Silicon	ppm	1180	1173
Sodium	ppm	26	34
Potassium	ppm	81	108
Calcium	ppm	59	66

This analysis was supplied to us by CANMET

TABLE 5

Percentage Yields of Major Fractions of Bitumens

	30-IPPL-84	31-IPPL-84	26-AB-81 (44-1)	26-AB-81
Asphaltene	20.6	14.5	33.2	14.1
Soft resin	24.7	20.1	24.3	17.3
Hard resin	3.7	4.7	6.4	5.8
Aromatics	26.3	32.8	28.6	39.7
Saturates	24.2	27.8	7.2	22.8

TABLE 6

Elemental Analyses of the Fractions

	Asphaltene	Soft resin	Hard resin
30-IPPL-84			
C	85.36	86.22	83.88
H	8.24	9.74	9.53
N	0.65	0.90	0.95
S	4.02	2.93	2.95
O	1.73	0.21	2.69
H/C	1.15	1.35	1.36
31-IPPL-84			
C	85.40	86.59	84.82
H	8.73	9.84	9.86
N	1.00	0.56	0.59
S	3.80	2.87	2.76
O	1.07	0.20	1.97
H/C	1.22	1.36	1.39
26-AB-81 (44-1)			
C	78.7	81.9	80.1
H	7.6	9.1	8.8
N	1.3	0.9	0.9
S	7.4	6.0	5.8
O	5.1	2.0	4.3
H/C	1.15	1.33	1.32
26-AB-81			
C	78.1	81.7	80.6
H	7.8	8.9	9.4
N	1.2	1.0	1.0
S	7.6	6.4	5.9
O	5.2	2.0	3.2
H/C	1.20	1.31	1.39

Comparison of the fractions from the two IPPL heavy crudes (Table 5) shows that 30-IPPL-84, which is vacuum bottomed at +1050°F, contains greater amounts of asphaltene (20.6%) and total resins (28%), as compared to 31-IPPL-84, which is distilled at a lower temperature (+900°F). However, the amounts of aromatics and saturates were less in the former than in the latter.

Athabasca vacuum bottom (26-AB-81-44-1), which is vacuum bottomed at +977°F, contains much more asphaltene (33.2%) and total resins (30.7%), as compared to the straight Athabasca bitumen (asphaltene = 14% and total resins = 23.1%). The lower boiling aromatics and saturates are present in larger amounts in straight bitumen as compared to the distilled bitumen.

In all of the cases soft resin is present at a much higher percentage than hard resin. The saturated hydrocarbons are present in lower quantities than the aromatics.

Elemental analyses were carried out for three fractions, and the results are presented in Table 6. As observed in our earlier work [1-4], asphaltene has the highest aromaticity of all the fractions, followed by the resins.

Asphaltene from 30-IPPL-84, which has been distilled at a higher temperature (+1050°F), is more aromatic (H/C = 1.15) than the asphaltene obtained from 31-IPPL-84. The same was true in the case of Athabasca asphaltenes. Asphaltene obtained from vacuum distilled heavy crude (26-AB-81-44-1) is more aromatic (H/C = 1.15) than the straight crude (H/C = 1.20).

Resin is the next most aromatic compound present in the heavy crudes. It was observed that the degree of aromaticity of the resins is almost the same for all the four sources. It was also found that the soft and hard resins have almost the same aromaticity values except for straight Athabasca resin.

Elemental analyses of the heteroatoms show that in all cases sulphur is present in quite large amounts in asphaltenes and resins, followed by oxygen and then nitrogen.

Although both of the resins contain the same amount of nitrogen, the hard resin contains more oxygen and less sulphur as compared to the soft resin.

It is interesting to observe that the amounts of heteroatoms in the Athabasca straight bitumen fractions and distilled bitumen fractions are almost the same.

PART II: KINETICS OF COKE FORMATION FROM FRACTIONS OF HEAVY CRUDES UNDER HYDROGEN

Kinetic Procedure

The object of the work was to study the kinetics of coke formation from crudes, and from asphaltenes and soft resins under an atmosphere of hydrogen.

The experiments were carried out in a specially designed stainless steel microreactor, shown with its accessories in Figure 12. It has a volume of 15 cm^3 and a mass of 756 g. A special balance, capable of weighing the microreactor and its contents with a precision of 0.01 g, was employed. The microreactor operated at a hydrogen pressure of up to 30 MPa and at temperatures up to 500°C. One thermocouple was inserted into the salt bath to control the temperature of the heating system, and another was inserted into the thermowell of the microreactor to measure the temperature of the reaction mixture.

The sample was thoroughly mixed with hydrogen with the help of an up-and-down agitating system. The reactor was connected to a variable-speed motor, the speed of which was maintained at 800 strokes per minute in all the experiments.

The reactor was heated to the required temperature by raising a pre-heated salt bath up to the reactor, by means of a hydraulic jack. The contents of the reactor rapidly attained the required temperature, reaching 450°C within 3 min. The agitation of the reactor in the salt bath caused the heating to be uniform throughout the system.

About 1 g of each sample was introduced into the reactor, which was weighed before and after the sample was added. Hydrogen was then admitted to the reactor, the final pressure usually being 15 MPa (2250 p.s.i); the reactor was then sealed by closing the valves. The system was agitated for

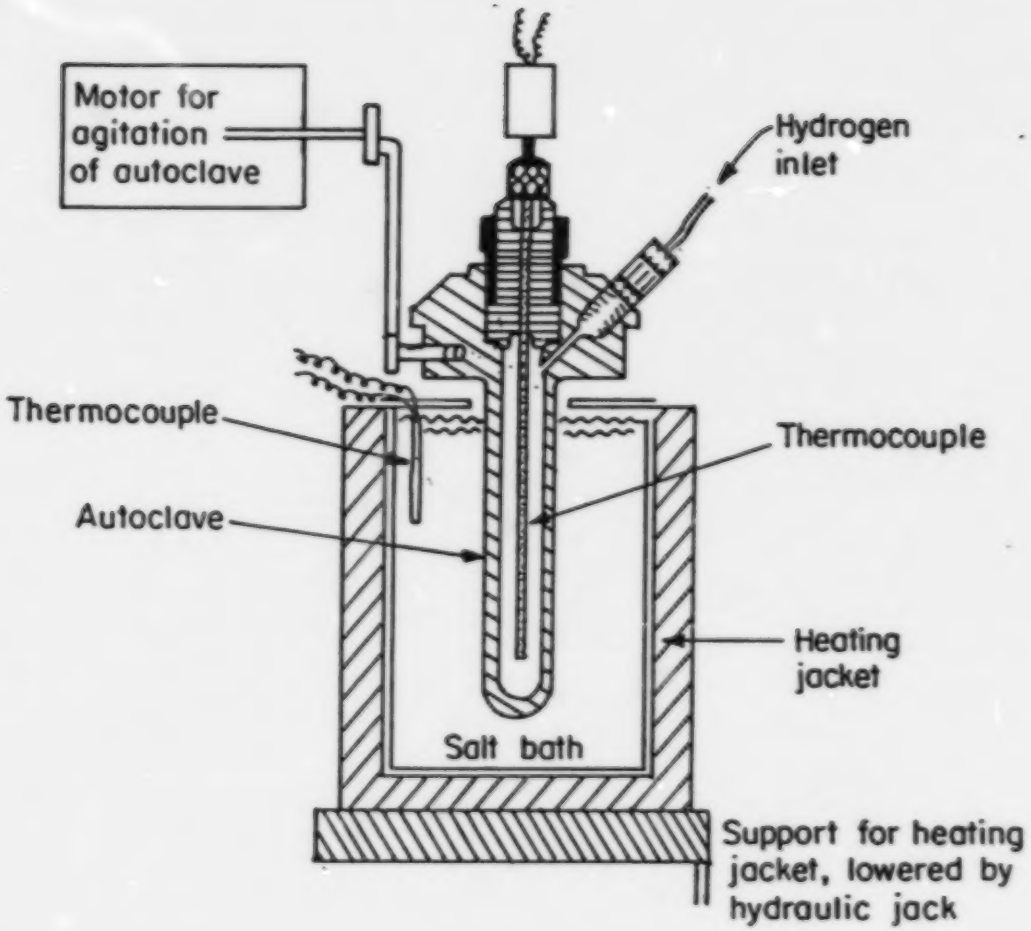

FIGURE 12: Specially designed stainless steel microreactor used in the kinetic experiments.

some time before being placed in the salt bath, and it was further agitated in the salt bath at the predetermined temperature.

At the conclusion of the reaction period the reactor was rapidly cooled (within 2 minutes) to room temperature by replacing the salt bath with a water bath and passing cold water through the system. The reactor was vented and then weighed, and the contents carefully removed by toluene extraction. The toluene extract was filtered in a weighed sintered crucible by means of a vacuum pump.

The crucible and the reactor were both washed with toluene and dried in an oven at 120°C for some time, then weighed to determine the amount of coke formed. Each experiment was repeated at least twice and the reproducibility of these results was within ± 3 wt%.

Results

Kinetic measurements for each whole bitumen and two of its fractions, asphaltene and soft resin, were carried out at temperatures ranging from 380° to 480°C, and at contact times from 15 minutes to 60 minutes, in the presence of hydrogen at 15 MPa.

The amounts of toluene-insoluble coke formed, with respect to the feed, from different fractions of IPPL heavy crudes, are listed in Tables 7 to 12, and for Athabasca vacuum bottom fractions in Tables 13 to 15. The variations of coke formation as a function of time and temperature for the various fractions are shown in Figures 13 to 21. The total amount of residue obtained was 93 to 96% of the feed; the rest consisted of volatile products.

Discussion

Our previous investigations [1-4] showed that in all cases asphaltene produced much more coke than the resins. The same was found in the present study.

TABLE 7

Kinetic Results for Coke Formation:

Asphaltene from 30-IPPL-84 Bitumen

Temperature/°C	Time/min.	Coke/wt%
380	15	NIL
380	30	NIL
380	45	7.1
400	15	16.8
400	30	23.5
400	45	29.2
400	60	30.7
410	15	35.1
410	30	42.4
410	45	46.8
410	60	46.9
420	15	45.2
420	30	52.3
420	45	54.4
420	60	54.9
440	30	54.1

All experiments done in duplicate.

No. of experiments = 32

TABLE 8

Kinetic Results for Coke Formation

Soft Resin from 30-IPPL-84 Bitumen

Temperature/°C	Time/min.	Coke/wt%
380	30	NIL
400	15	NIL
400	30	NIL
400	45	NIL
410	30	NIL
420	15	NIL
420	30	4.1
420	45	7.8
420	60	9.9
440	15	8.6
440	30	12.8
440	45	14.9
440	60	17.5
460	15	15.6
460	30	19.5
460	45	24.8
460	60	25.5
480	15	26.1
480	30	35.3
480	45	36.5
480	60	36.2

All experiments done in duplicate.

No. of experiments = 42

TABLE 9

Kinetic Results for Coke Formation

30-IPPL-84 Bitumen

Temperature/°C	Time/min.	Coke/wt%
380	30	NIL
380	60	NIL
400	15	NIL
400	30	4.1
400	45	7.2
400	60	8.8
420	15	6.2
420	30	10.4
420	45	14.3
420	60	17.7
440	15	17.5
440	30	23.6
440	45	26.1
440	60	28.0
460	15	20.4
460	30	26.4
460	45	27.3
460	60	30.2

All experiments done in duplicate.

No. of experiments = 36

TABLE 10

Kinetic Results for Coke Formation

Asphaltene from 31-IPPL-84 Bitumen

Temperature/°C	Time/min.	Coke/wt%
380	15	NIL
380	30	NIL
380	45	7.5
400	15	19.2
400	30	25.8
400	45	31.0
400	60	31.8
410	15	24.1
410	30	31.1
410	45	38.6
410	60	40.8
420	15	41.1
420	30	50.5
420	45	52.6
420	60	52.8
440	30	52.2

All experiments done in duplicate.

No. of experiments = 32

TABLE 11

Kinetic Results for Coke Formation

Soft Resin from 31-IPPL-84 Bitumen

Temperature/°C	Time/min.	Coke/wt%
400	15	NIL
400	30	NIL
400	45	NIL
410	30	NIL
420	15	NIL
420	30	6.5
420	45	10.3
420	60	12.5
440	15	9.9
440	30	16.9
440	45	19.3
440	60	22.3
460	15	18.2
460	30	26.6
460	45	31.1
460	60	33.2
480	15	22.2
480	30	33.9
480	45	35.4
480	60	35.1

All experiments are in duplicate.

No. of experiments = 40

TABLE 12

Kinetic Results for Coke Formation

31-IPPL-84 Bitumen

Temperature/°C	Time/min.	Coke/wt%
400	15	NIL
400	30	NIL
400	45	2.2
400	60	5.8
420	15	NIL
420	30	7.2
420	45	9.9
420	60	13.7
440	15	7.9
440	30	12.3
440	45	14.9
440	60	16.2
460	15	11.1
460	30	17.8
460	45	21.2
460	60	22.0

All experiments done in duplicate.

No. of experiments = 32

TABLE 13

Kinetic Results for Coke Formation

Asphaltene from 26-AB-81(44-1) Bitumen

Temperature/°C	Time/min.	Coke/wt%
380	15	NIL
380	30	NIL
380	45	2.4
400	15	8.6
400	30	13.8
400	45	19.4
400	60	21.8
420	15	17.3
420	30	23.3
420	45	25.6
420	60	26.9
440	15	23.8
440	30	29.3
440	45	31.1
440	60	32.0
460	15	34.8
460	30	40.0
460	45	41.0
460	60	40.8

All experiments done in duplicate.

No. of experiments = 38

TABLE 14

Kinetic Results for Coke Formation

Soft Resin from 26-AB-81(44-1) Bitumen

Temperature/°C	Time/min.	Coke/wt%
400	45	NIL
400	60	NIL
410	30	NIL
410	45	NIL
420	15	9.9
420	30	18.8
420	45	23.6
420	60	26.4
440	15	21.3
440	30	26.6
440	45	28.7
440	60	30.1
460	15	30.3
460	30	35.7
460	45	37.8
460	60	37.3
480	15	34.9
480	30	40.2
480	45	40.8
480	60	40.5

All experiments done in duplicate.

No. of experiements = 40

TABLE 15

Kinetic Results for Coke Formation:

26-AB-81 (44-1) Bitumen

Temperature/°C	Time/min.	Coke/wt%
400	15	NIL
400	30	7.5
400	45	9.9
400	60	11.5
420	15	9.1
420	30	15.8
420	45	16.6
420	60	18.6
440	15	14.1
440	30	17.5
440	45	20.9
440	60	21.4
460	15	18.8
460	30	23.7
460	45	26.4
460	60	27.3

All experiments done in duplicate.

No. of experiments = 32

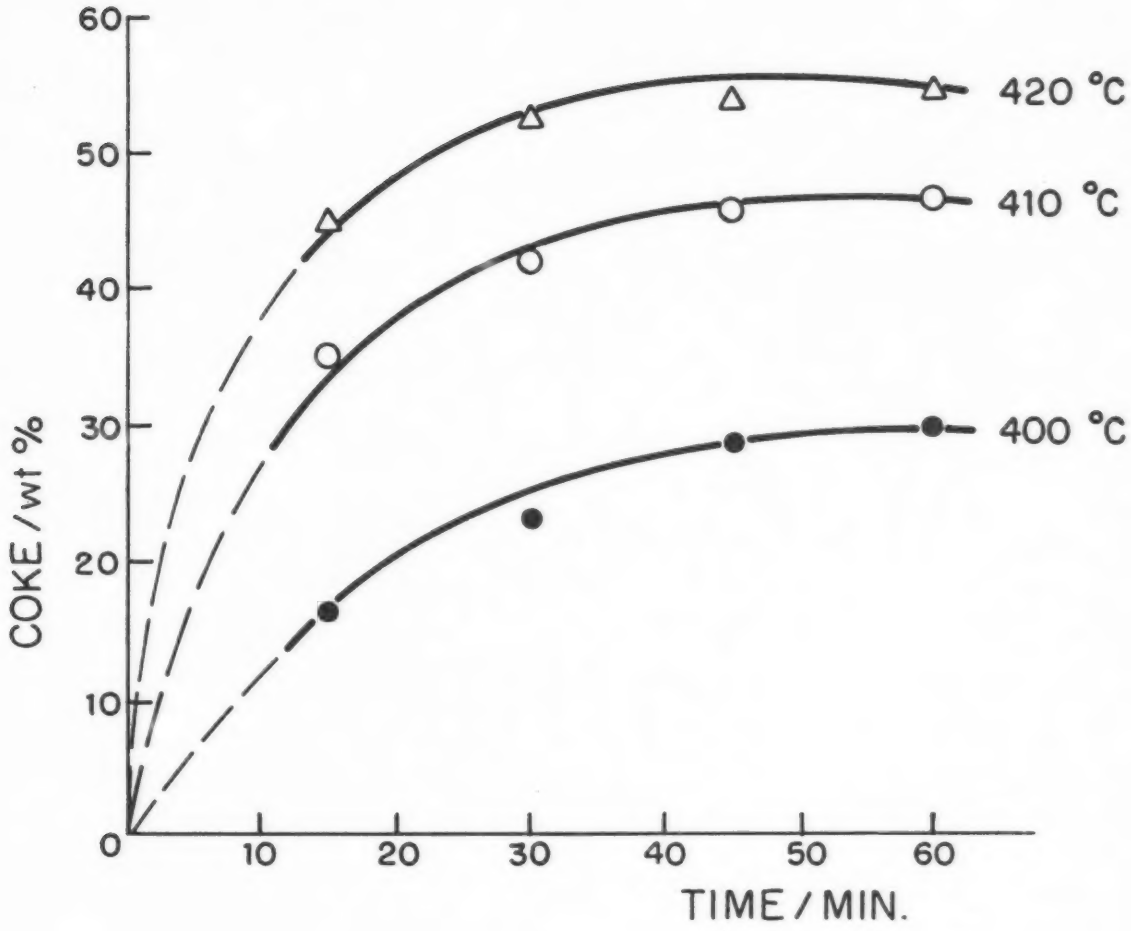

FIGURE 13: Plots of coke formed as a function of time, for asphaltene from 30-IPPL-84 bitumen, at three temperatures.

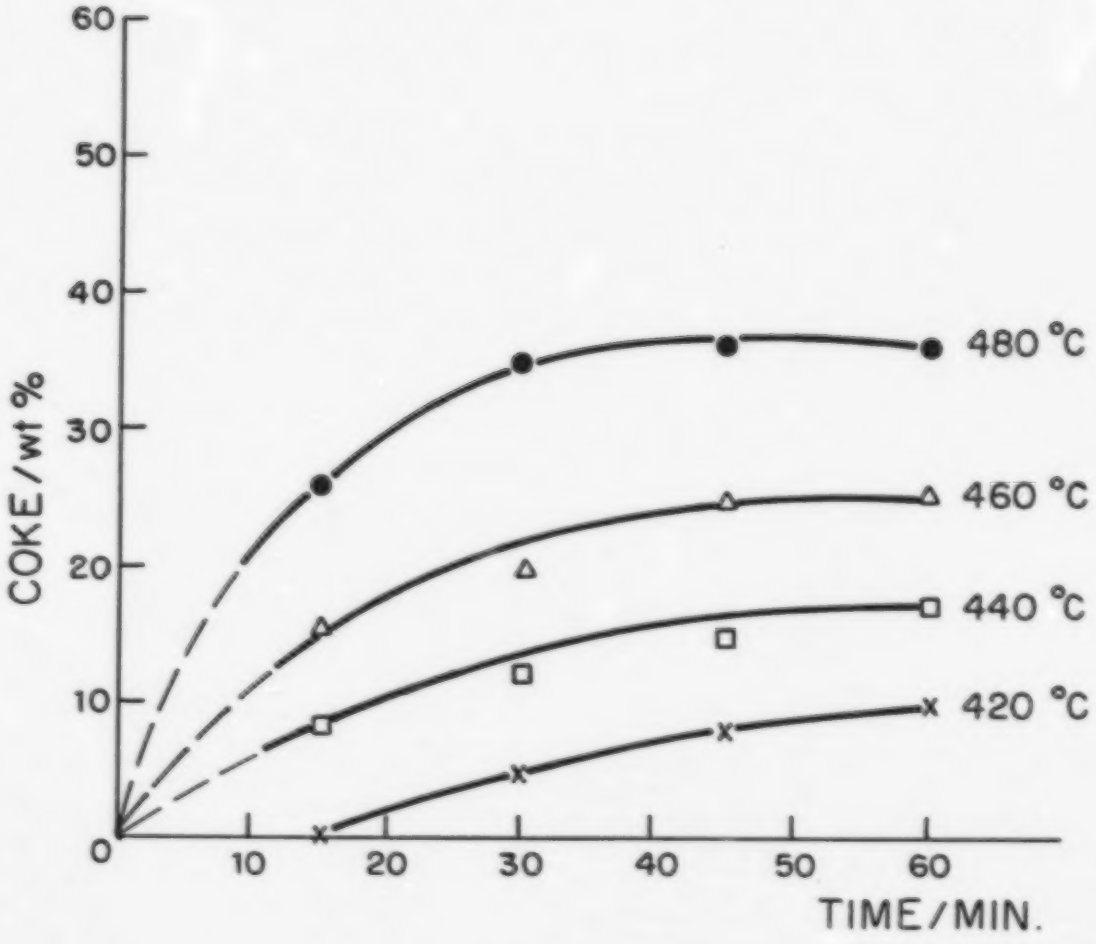

FIGURE 14: Plots of coke formed as a function of time, for soft resin from 30-IPPL-84 bitumen, at four temperatures.

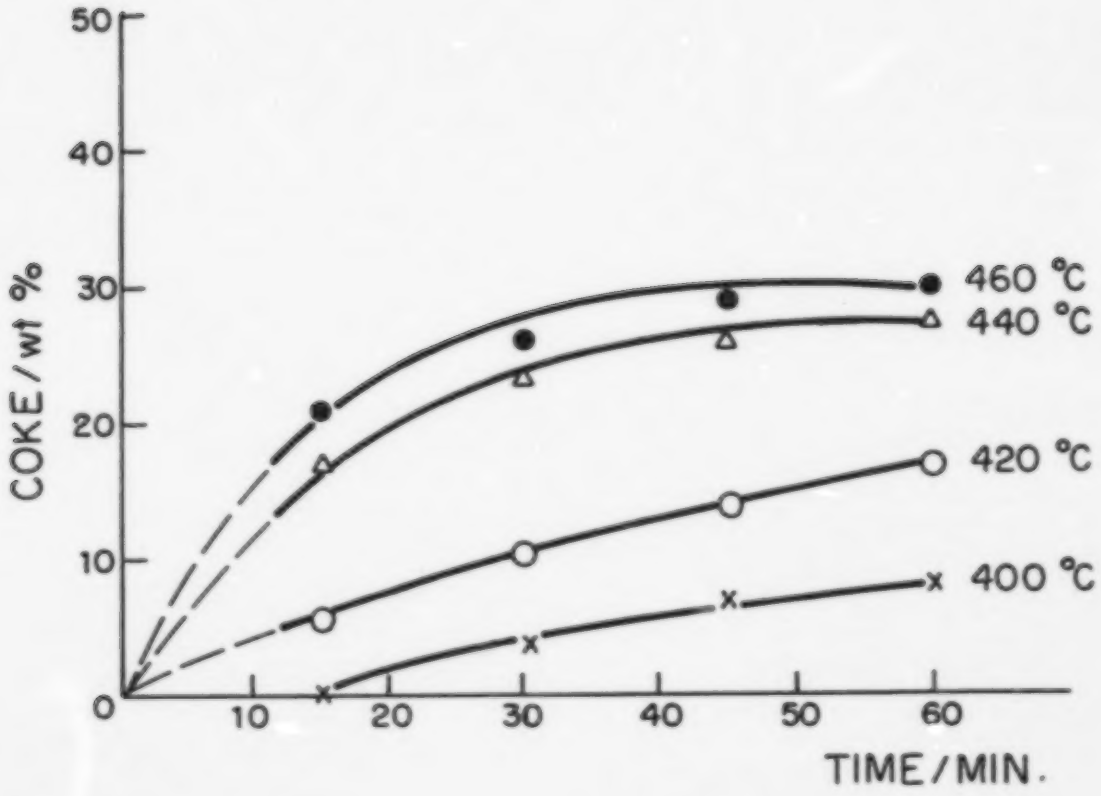

FIGURE 15: Plots of coke formed as a function of time, for 30-IPPL-84 bitumen, at four temperatures.

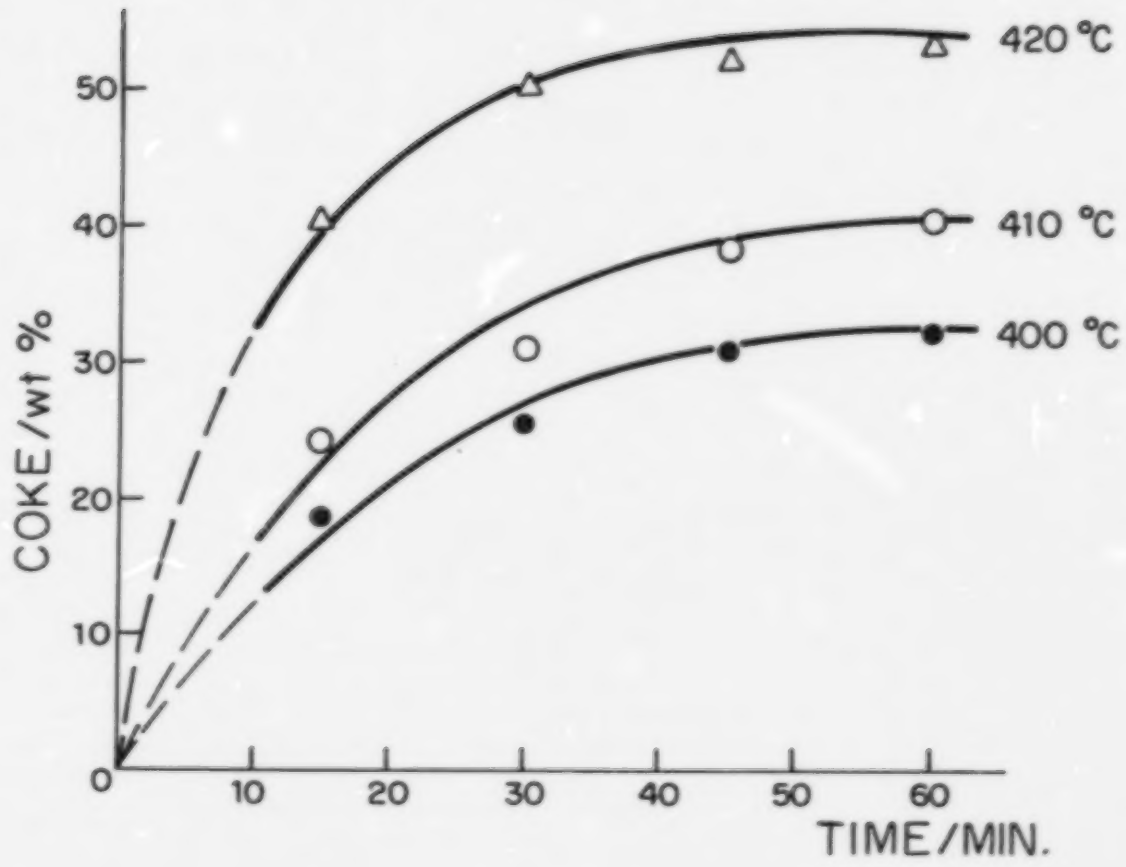

FIGURE 16: Plots of coke formed as a function of time, for asphaltene from 31-IPPL-84 bitumen, at three temperatures.

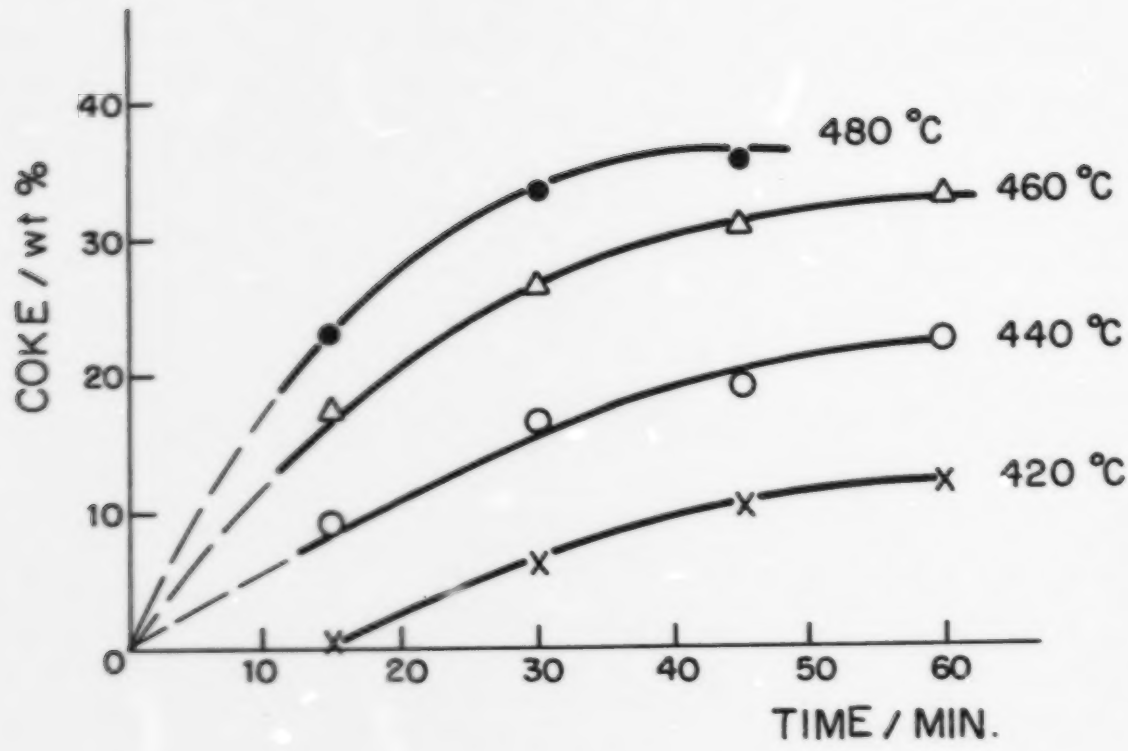

FIGURE 17: Plots of coke formed as a function of time, for soft resin from 31-IPPL-84 bitumen, at four temperatures.

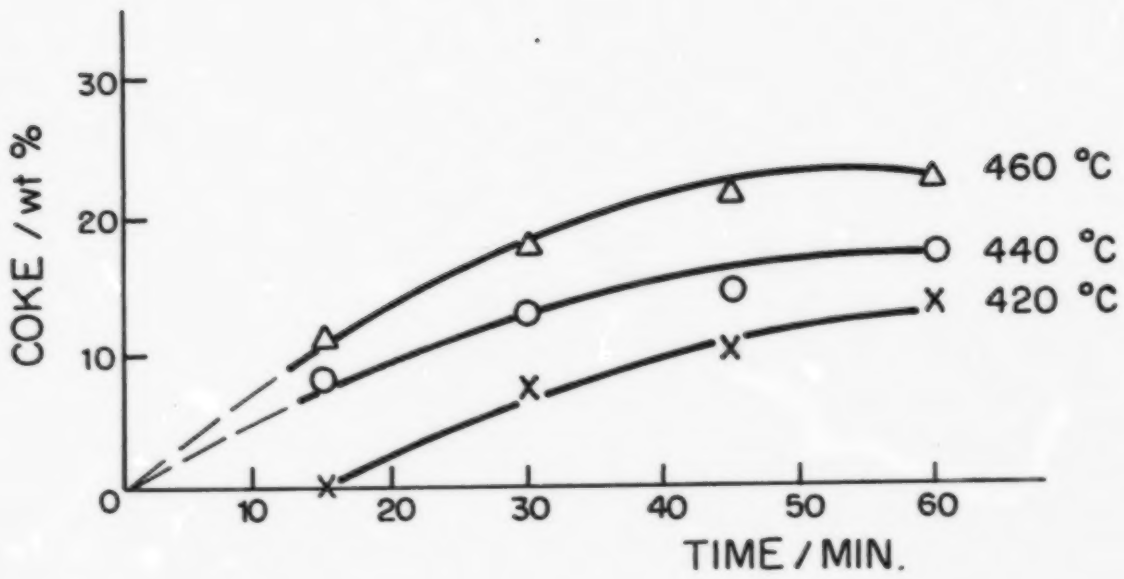

FIGURE 18: Plots of coke formed as a function of time, for 31-IPPL-84 bitumen, at three temperatures.

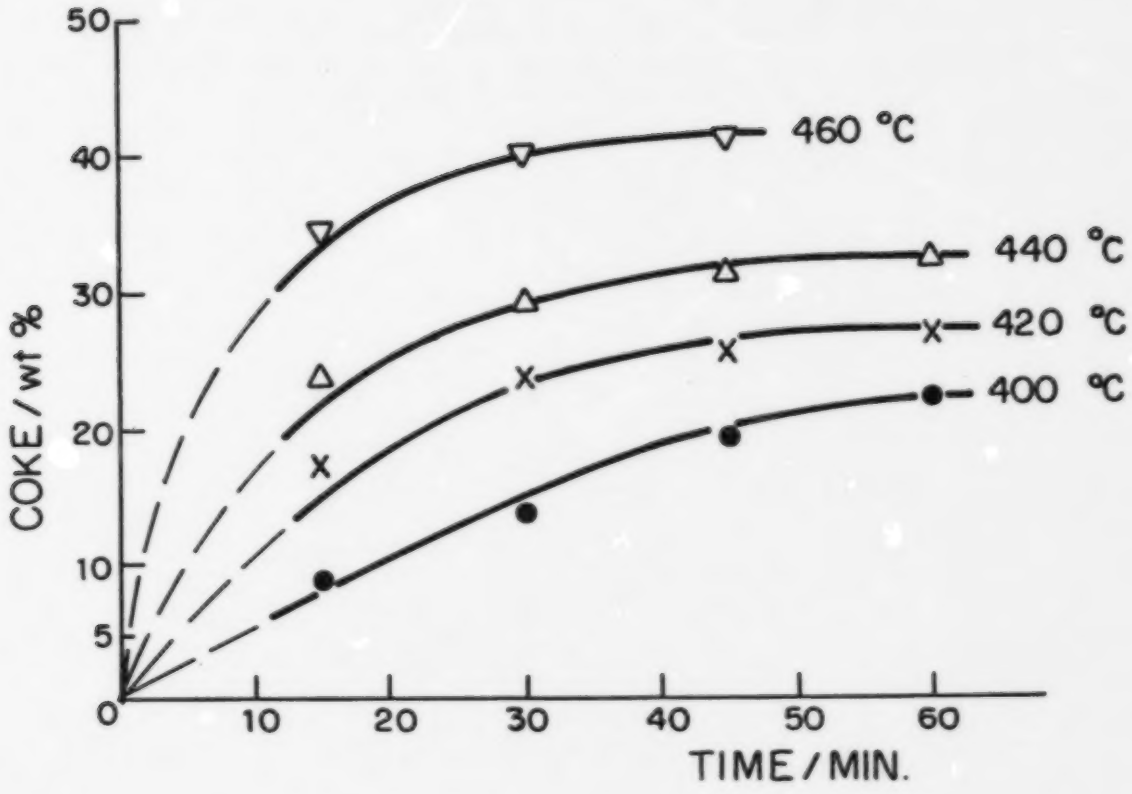

FIGURE 19: Plots of coke formed as a function of time, for asphaltene from 26-AB-81 (44-1) bitumen, at four temperatures.

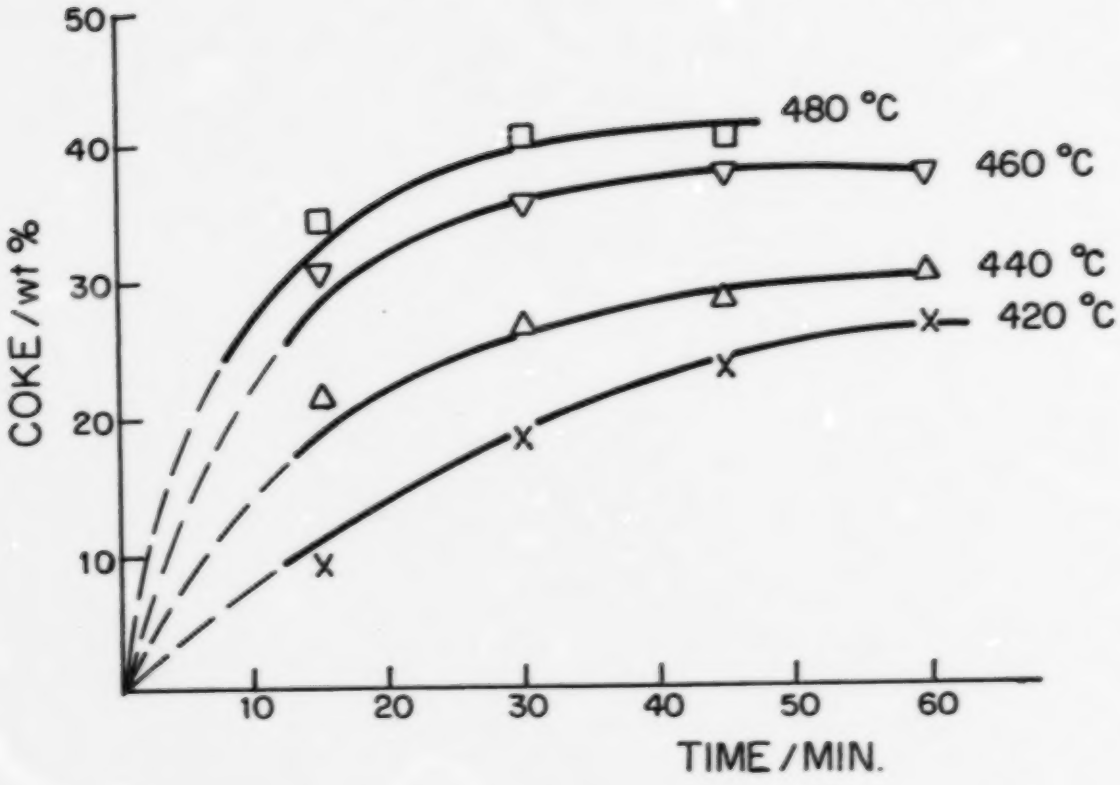

FIGURE 20: Plots of coke formed as a function of time, for soft resin from 26-AB-81 (44-1) bitumen, at four temperatures.

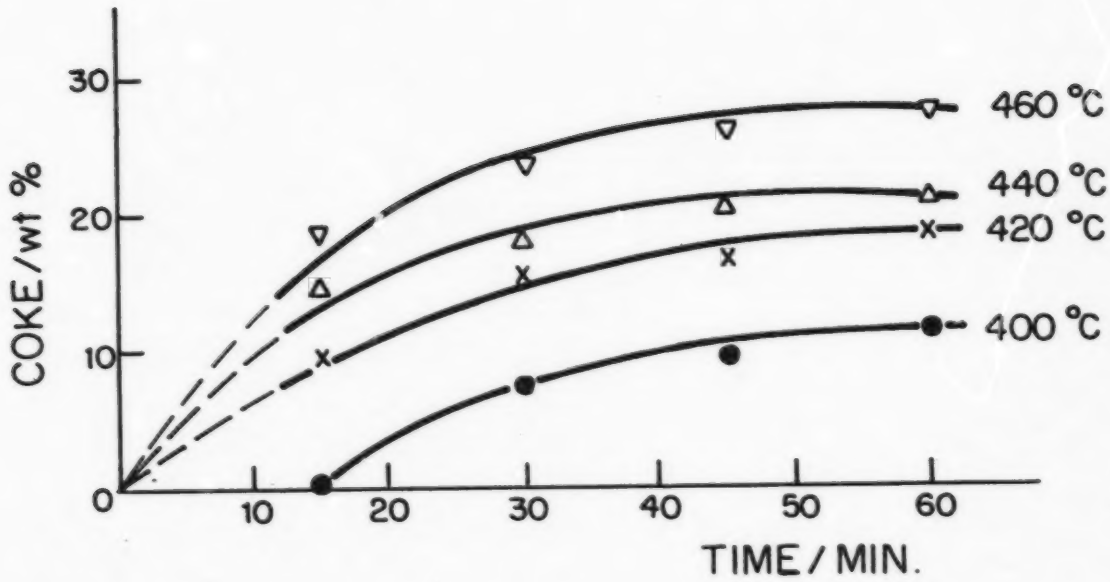

FIGURE 21: Plots of coke formed as a function of time, for 26-AB-81 (44-1) bitumen, at four temperatures.

It is interesting to observe that asphaltene from 30-IPPL-84 heavy crude is more aromatic as compared to asphaltene from 31-IPPL-84, but produced less coke at 400°C and much more coke at 410°C. There was a sudden increase in the amount of coke formation from 400° to 410°C for asphaltene from 30-IPPL-84, and the same was true for the asphaltene of 31-IPPL-84 from 410° to 420°C. This difference in the behaviour of the two asphaltenes needs further investigation.

Although the aromaticities of the soft resins from two IPPL sources were almost the same, soft resin from 31-IPPL-84 bitumen produced much more coke than the soft resin from 30-IPPL-84, under all conditions. This behaviour of the asphaltene and resins may be due to structural differences.

As far as the bitumens themselves are concerned, comparison of Figures 12 and 15 shows that in all cases 30-IPPL-84 heavy crude, which is more aromatic, produced much more coke than the 31-IPPL-84 heavy crude.

It is concluded, as in the previous work [1-4], that asphaltene is mainly responsible for coke formation, followed by the resins. 30-IPPL-84 heavy crude has much more asphaltene (20.6%) and total resins (28.4%) than the 31-IPPL-84 heavy crude. It therefore seems clear that the large amounts of asphaltene and resins are also responsible for the fact that more coke is obtained from 30-IPPL-84 heavy crude.

First-order rate constants for coke formation from two fractions and whole heavy crudes are presented in Tables 16 to 18.

It is to be noted that the rate constants for IPPL-asphaltenes are much higher than those for the corresponding resins. The rate constant for soft resin at 440°C is lower than that for asphaltene at 400°C. The asphaltene from 30-IPPL-84 is more aromatic than that of 31-IPPL-84 and the rate constants are also higher. Thus it is clear, in agreement with our previous conclusion [1-4], that aromaticity plays an important role in coke

TABLE 16

First-Order Rate Constants

30-IPPL-84 Heavy Crude and its Fractions

Temperature/°C	Asphaltene	Resin	Crude
400	0.038	-	-
410	0.068	-	-
420	0.090	-	0.017
440	-	0.033	0.044
460	-	0.040	0.060
480	-	0.064	-

TABLE 17

First-Order Rate Constants for Coke Formation

31-IPPL-84 Crude and its Fractions

Temperature/°C	Asphaltene	Resin	Crude
400	0.036	-	-
410	0.041	-	-
420	0.080	-	-
440	-	0.025	0.028
460	-	0.035	0.037
480	-	0.053	-

TABLE 18

First-Order Rate Constants for Coke Formation

Athabasca Vacuum Bottom and its Fractions

Temperature/°C	Asphaltene	Resin	Crude
400	0.025	-	-
420	0.038	0.029	0.032
440	0.050	0.046	0.051
460	0.106	0.076	0.053
480	-	0.086	-

formation.

Our conclusion that asphaltene and the resins are mainly responsible for coke formation is supported by a comparison of the results with 30-IPPL-84 and 31-IPPL-84 heavy crudes. The former, which has more asphaltenes and resins than the latter (Table 5), shows higher rates of coke formation (Table 16).

It is interesting to observe that Athabasca asphaltene has a much lower rate of coke formation than 30-IPPL-84 asphaltene, although the H/C ratio is the same (1.15). On the other hand, Athabasca soft resin has a much higher rate of coke formation than that of IPPL soft resins, though the aromaticity values are almost the same.

Table 19 shows a comparison between the present results and those obtained in previous investigations [1-4]. It is to be noted that asphaltene from Athabasca bottom product produces a similar amount of coke to asphaltene from Cold Lake bitumen and from Light Arabian vacuum bitumen. Much larger amounts, however, are produced from asphaltene from the two Interprovincial Pipeline crudes. The amounts of coke produced from the soft resins are similar to one another, apart from the smaller amounts given by Interprovincial Pipeline vacuum bottom (+ 900°F).

TABLE 19

Comparison of First-Order Rate Constants at 420°C

	Crude	Asphaltene	Resin
Interprovincial Pipeline vacuum bottom(+1050°F)	0.021	0.090	0.025
Interprovincial Pipeline vacuum bottom(+900°F)	0.020	0.080	0.015
Athabasca bottom products (977°F)	0.032	0.038	0.029
Cold Lake bitumen*	-	0.036	0.024
Light Arabian vacuum* bitumen	-	0.040	0.021

* Results quoted in the previous report [2]. In that work kinetic measurements were not made on the bitumens themselves.

APPENDIX: SEPARATION PROCEDURES

The separation procedures were considered in detail in the previous report [2]; for convenience they are summarized here.

According to ASTM-D2006, deasphaltenation of bitumen is carried out by precipitation with 40 times its volume of n-pentane; n-heptane is also recommended for this purpose. The following method [9] was found to give highly reproducible results:

5 g of bitumen was dissolved in 5 mL of benzene in a conical flask. To this was added 200 mL of n-pentane (HPLC grade, from Fisher Scientific), with thorough shaking. The flask was kept in the dark for 10 hours with occasional shaking. The contents were then filtered through a sintered crucible, and the precipitate washed with n-pentane as long as a clear solution was obtained. The n-pentane extract was kept for later treatment. The precipitate in the crucible was dissolved in a minimum amount of benzene which was then distilled under vacuum. The material was then kept for half an hour at 100°C, after which it was completely dry. Since asphaltene is sensitive to atmospheric oxygen, care was taken not to expose it to the atmosphere for too long. The dark brown precipitate, consisting of asphaltene, was weighed and its yield calculated; it was then stored in a vacuum desiccator. Since this procedure is very sensitive to factors such as the quantity of n-pentane used, the temperature, and the time taken to perform the operations, care was taken to reproduce the conditions in subsequent separations. Experiments were repeated about ten times, with reproducibility of ± 1.5%.

Further separation of the n-pentane extract was carried out by the technique of adsorption column chromatography. Maltene was first separated into resins and oil by the Syncrude analytical method (also recommended in

ASTM-D-2007-80), a benzene-acetone 50/50 mixture being used as eluent. Attapulgus clay was used as the adsorbing material. The commercial attapulgus clay, grade AX-1799, was supplied by Matheson, Coleman and Bell, Manufacturing Chemists, Norwood, Ohio. This clay, in the form of a fine powder, was pressed hydraulically and the cake formed was crushed, the resulting fine particles being sieved to 30-60 mesh. It was then activated at 300°F for 3 hours, transferred hot into a closed bottle and kept in a desiccator for further use.

A 65 mL volume of the activated clay was packed into the chromatographic column of the recycling system. The apparatus consisted of a 500 mL kettle having two necks. The chromatographic column (22 x 450 mm in size), with an insulated jacket, was mounted on one neck; a distillation tube was on the other neck. A condenser was attached at the top of the column, which is also connected to the distillation tube by means of a side arm. The kettle was heated by a mantle having a temperature-controlled system. Thermostatted hot water at the required temperature was circulated through the jacket of the distillation tube, in order to allow the vapour from the kettle to reach the condenser. The condensed liquid dropped into the chromatographic column and finally entered the kettle, the required compound being eluted. Recycling thus is accomplished. After the elution of one component another solvent was placed in the kettle, in order to extract another component; the process was continued in this way.

The n-pentane extract, after removal of asphaltene, was concentrated to about 20 mL by evaporating the solvent in a rotary evaporator. The clay in the column was treated with 50 mL of n-pentane, and the concentrated maltene solution added to it. The kettle was charged with 200 mL of n-pentane, and the concentrated maltene solution added to it. The kettle was charged with 200 mL of n-pentane and refluxing continued for 2 hours; the

n-pentane elutes the oil and returns to the kettle. When all of the oil was eluted, the system was cooled, the kettle replaced, and the column dried by purging with nitrogen. The column now retained the resins.

The kettle was next replaced by another kettle containing 200 mL of methyl ethyl ketone (MEK) of high purity (obtained from Fisher Scientific), and the system was refluxed for 2 hours. Methyl ethyl ketone extracts soft resin from the clay, and hard resin is retained in the column. After the soft resin elution was completed, the column was dried by nitrogen as before.

The kettle was again replaced with another kettle containing 200 mL of tetrahydrofuran (histological grade, obtained from Fisher Scientific) and 10 mL distilled water (added to prevent explosion due to peroxide formation). Tetrahydrofuran (THF) extracts hard resin from the column and returns to the kettle, the whole operation taking about 2 hours. A change in colour of the THF solution indicated when the extraction was complete.

The MEK and THF extracts were evaporated in a rotary evaporator under vacuum to the minimum possible amount. They were then transferred to evaporating dishes, and the rest of the solvent evaporated, over a long period, in a vacuum desiccator. The resins were finally dried completely in an oven at 100°C for 10 minutes, and then kept in a closed bottle which was placed in a vacuum desiccator. The yield was determined.

The soft resin was obtained as a dark coloured highly dense oily liquid. The hard resin was a dark coloured crystalline semi-solid.

The pentane extract obtained from the clay, containing oil, was further fractionated into aromatics and saturated hydrocarbons. The aromatic portion usually contains polycondensed aromatic rings with aliphatic side chains. The saturated fraction is mainly naphthenic in nature with some long-chain paraffins.

The separation of oil was carried out by the ASTM-D1319-70 method, with modifications according to ASTM-D2549-81. A chromatographic column (900 x 10 mm) was filled with 60 mL of activated silica gel (100 - 200 mesh, grade 923) obtained from Davison Chemicals, Baltimore, Maryland. Above the silica gel was another 5 mL of activated alumina of grade AX-0612-3, type F-20, 800-200 mesh, obtained from MCB Manufacturing Chemists, Cincinnatti, Ohio. Silica gel and alumina were both activated each time prior to use, by heating to 300°F for 3 hours. The column was first filled with n-pentane, to which silica gel was added slowly with continuous vibration of the column; care was taken to avoid any air gap inside the packed column. Alumina was then added by following a similar procedure. Uniform packing throughout the column length was then achieved by gentle admission of nitrogen at a slightly increased pressure. Care was taken to prevent the pentane level from falling below the alumina.

The oil containing the pentane extract was concentrated to about 5 mL in a rotary evaporator. This liquid was then injected into the alumina by means of a syringe. The column was then eluted with 200 mL of n-pentane by applying a gentle nitrogen pressure through the column; this helps to avoid any channelling of the column and also gives a uniform flow of liquid. The pentane carried the saturated portion with it, the aromatic portion being retained inside the packing material. Since saturates are colourless, the pentane solution was clear. The completion of the elution was tested by ultraviolet spectrophotometry.

Since aromatics are coloured, it was easy to observe that they are retained in the column, and that they do not contaminate the saturates. The aromatics were eluted from the column with approximately 80 mL of toluene; the complete elution of the aromatics was easily observed visually.

The pentane and toluene were both evaporated from the compounds in a rotary evaporator. The residues were dried in an oven at 100°C for half an hour. The dried material was weighed and its yield calculated.

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